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(54) ENZYME-CONTAINING GRANULE

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to enzyme-containing granules adapted for use in fabric-washing detergent compositions, and to fabric-washing detergent compositions containing such granules.

The expression "fabric-washing detergent composition" is used herein to include not only detergent compositions adapted for use in aqueous solution during an actual fabric-washing procedure, and for the dual purposes of acting in aqueous solution as a pre-wash soaking medium and as a washing medium, but also detergent compositions primarily adapted for use in aqueous solution as a pre-wash soaking medium prior to the use of a different fabric-washing detergent composition during a subsequent fabric-washing procedure.

Fabric-washing detergent compositions incorporating enzymes have been produced in quantity during recent years. Numerous special methods have been proposed for incorporating enzymes into such compositions, as the presence of free enzymes in detergent compositions could be a health hazard to the manufacturer of the detergent compositions and to a subsequent user of the detergent compositions, and also enzymes are susceptible to moisture and to many of the ingredients in conventional detergent compositions and are thereby liable to degradation during storage.

Quite correctly, the health hazard associated with enzymes has always been considered to be the more important problem, and considerable effort has been expended in making enzymatic detergent compositions which, when used under normal conditions, produce no danger to the manufacturer or to the user. As a result of this effort, it is now possible to produce enzymatic detergent compositions which are satisfactory as far as this aspect is concerned. However, it has been found that the best solutions to the health hazard problem are not necessarily also the best methods for maintaining the stability of the enzyme during storage.

Usually, enzymes are obtained commercially in the form of powders which are mixtures of the enzyme itself with one or more inert diluents. This enzyme powder cannot be put directly into a conventional detergent composition without degradation and health hazard problems, and one of the commonest ways of incorporating the enzyme powder into a detergent composition is in the form of a granule. Such a granule typically comprises a core on to which the enzyme powder is adhered. By being adhered to the core, the enzyme powder is less likely to be found free in the detergent composition and thus, for instance, the risk of the enzyme powder being inhaled by a manufacturer or a user of the detergent composition is very much reduced. Preferably, the enzyme powder on the core is covered by a layer of material which further reduces the risk of the enzyme powder becoming free. Nonionic organic compounds have been recognised as being very suitable materials for making up this layer, and also for adhering the enzyme powder to the core. Enzymes may also be obtained commercially in liquid form, wherein the inert diluents are liquids such as nonionic organic compounds. It is desirable that an enzyme-containing granule prepared from an enzyme slurry should be given an outer layer of material similar to that applied to an enzyme-containing granule prepared from an enzyme powder.

Although a detergent composition incorporating such granules is very satisfactory as far

as the health hazard problem is concerned, the stability of the enzyme towards degradation during storage is not wholly satisfactory and considerable loss of enzyme activity can occur.

By the present invention it has been found that the storage stability of an enzyme incorporated in a granule as described above can be considerably enhanced if the granule also incorporates a polymer as defined below. The favourable properties of the granule in safeguarding the health of a manufacturer or a user of the detergent composition are in no way reduced by the presence of the polymer.

According to the invention, an enzyme-containing granule comprises a core of carrier material which is a solid, water-soluble inorganic alkali metal salt, an enzyme, affixed to the core by means of a cohesive nonionic detergent with a melting point in the range of 0–30°C enrobing the core, and an enrobing outer layer comprising a polymer as defined below.

The polymer comprises from about 0.1 to about 5%, and particularly from about 0.5 to about 3%, by weight of the enzyme-containing granule.

In one embodiment of the invention, the enzyme is in the form of a powder and is adhered to the core by means of a layer of cohesive nonionic detergent applied to the core prior to the application of the enzyme powder.

In an alternative embodiment of the invention, the enzyme is in the form of an enzyme nonionic detergent slurry, which enzyme slurry diluted as necessary is applied directly onto the core.

An outer layer of cohesive nonionic detergent material in which the polymer is incorporated is applied to the enzyme-coated core.

The invention includes a process for the preparation of an enzyme-containing granule according to the invention.

In particular the invention includes a process for the preparation of an enzyme-containing granule, in which process cohesive nonionic detergent is sprayed at a temperature of 30–60°C onto a granulated core material as hereinbefore defined, enzyme powder is applied to this treated granulated core material to produce an enzyme-containing granule, and subsequently the enzyme-containing granule is sprayed with a mixture of cohesive nonionic detergent and a polymer as defined below at a temperature of 50–70°C.

The invention also includes a fabric-washing detergent composition incorporating enzyme-containing granules according to the invention.

The polymer for use in an enzyme-containing granule of the invention is a polymer of an unsaturated mono- or polycarboxylic acid, or a copolymer of these with another, different unsaturated monomer. Hereinafter, the expression "polymer" is used to cover both the polymers, obtained by polymerization of the unsaturated mono- or polycarboxylic acids, as well as the copolymers, obtained by copolymerization of the unsaturated mono- or polycarboxylic acids with another, different unsaturated monomer.

Suitable polymers are polyacrylic acid, -methacrylic acid, and -maleic acid.

Suitable unsaturated monomers for copolymerisation with the unsaturated mono- or polycarboxylic acids are alpha-olefins such as ethylene, propylene, iso-butylene, 1-butene, 2-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-octadecene and vinyl compounds such as styrene, α-methyl styrene, vinyl toluene, vinyl acetate, vinyl amine, vinyl chloride, vinyl formate, vinyl propionate, vinyl alkyl ethers such as methylvinylether, alkyl acrylates, alkyl methacrylates, acrylamides and alkylacrylamides.

Mixtures of any of these monomers may be used.

The polymers may be used in the acid form (including the anhydride form), or they may be converted into their partial alkali-metal salts, their amides and esters.

A particularly preferred polymer for use in accordance with the invention is a copolymer of a low-molecular weight olefin, such as ethylene, with an unsaturated dicarboxylic acid or its anhydride, such as maleic acid or maleic anhydride. The preparation of such copolymers is detailed in US patents Nos. 2,378,629, 2,396,785, 3,157,595 and 3,340,680. Several of these preferred copolymers, incorporating different quantities of the monomers and having different molecular weights, are commercially available. Generally, such copolymers incorporate from about 100 to about 5,000 monomer units, and have a molecular weight of from about 10,000 to about 500,000. Examples of suitable copolymers are those sold by Monsanto Chemicals under the trade names "EMA 11", "EMA 21" and "EMA 1103", which are believed to be 1:1 copolymers of ethylene and maleic anhydride of different molecular weights.

The core of the enzyme-containing granule of the invention is a solid water-soluble alkali metal inorganic salt. Salts which are also detergency builders are particularly suitable for this purpose. Examples of suitable inorganic salts are sodium tripolyphosphate, sodium orthophosphate, sodium pyrophosphate, sodium hexametaphosphate, sodium carbonate, sodium silicate, sodium bicarbonate, sodium tetraborate, sodium perborate, and sodium sulphate. Potassium salts may also be used, although these are not preferred. The material comprising the core must be non-friable, otherwise the core may be broken up during the preparation of the enzyme-containing granule, and a particle of the core material should also readily absorb

other materials of the enzyme-containing granule into its surface. Granular sodium tripolyphosphate has been found to be the most suitable material for use as the cores of enzyme-containing granules.

The cohesive nonionic detergent consists of one or more nonionic detergent-active compounds. Many nonionic detergent-active compounds are known, and are widely used for their detergent-active properties. However, not all known nonionic detergent-active compounds are suitable for use in enzyme-containing granules.

Opinions differ on the most preferred melting-point ranges for nonionic detergent-active compounds to be used in enzyme-containing granules. In enzyme-containing granules produced prior to the present invention, some manufacturers have preferred to use nonionic detergent-active compounds having melting points in the range of 45 to 95°C, and others have preferred to use nonionic detergent-active compounds having melting points in lower temperature ranges. The use of the higher melting-point nonionic detergent-active compounds gives enzyme-containing granules which are almost certain to be non-glutinous and free-flowing, but, as most enzyme-containing granules are prepared by a process which involves spraying nonionic detergent-active material onto a granular base, the higher melting-point nonionic detergent-active compounds are liable to solidify before coming into contact with the granular base and thus may form an imperfect covering on the granular base. On the other hand, the use of the lower melting-point nonionic detergent-active compounds usually results in a more perfect covering of the granular base, although it is possible that the flow properties of the sprayed granules may not be as good as those of granules prepared using the higher melting-point nonionic detergent-active compounds.

The enzyme-containing granules of the invention may incorporate either lower melting point or higher melting point nonionic detergent-active compounds, or mixtures of both types. However, for the purposes of the invention the nonionic detergent-active compounds used should have melting points in the range of about 0 to about 30°C, and particularly preferably 15 to 25°C.

Suitable nonionic detergent-active compounds fall into several different chemical types. These are generally polyoxyethylene condensates of organic compounds having reactive hydrogen atoms. Examples of suitable nonionic detergent-active compounds are:

(a) Polyoxyethylene condensates of aliphatic carboxylic acids, whether linear- or branched-chain and unsaturated or saturated, containing from about 8 to about 18 carbon atoms in the aliphatic chain and incorporating from 5 to about 50 ethylene oxide units. Suitable carboxylic acids include "coconut" fatty acid (derived from coconut oil) which contains on average about 12 carbon atoms, "tallow" fatty acid (derived from tallow-class fats) which contains on average about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid.

(b) Polyoxyethylene condensates of aliphatic alcohols, whether linear- or branched-chain and unsaturated or saturated, containing from about 8 to about 24 carbon atoms and incorporating from about 5 to about 50 ethylene oxide units. Alcohols containing about 8 to 18 carbon atoms, and condensates incorporating not more than about 20 ethylene oxide units, are preferred. Suitable alcohols include "coconut" fatty alcohol (derived from coconut oil), "tallow" fatty alcohol (derived from tallow-class fats), lauryl alcohol, myristyl alcohol and oleyl alcohol. A particularly preferred nonionic detergent-active compound for use in accordance with the invention is a material sold under the Registered Trade Mark "Tergitol 15-S-9", and other members of the "Tergitol" range may also be used.

(c) Polyoxyethylene condensates of alkyl phenols, whether linear- or branched-chain, wherein the alkyl chain contains about 6 to 18 carbon atoms, incorporating from about 5 to 50 ethylene oxide units. Alkyl phenols wherein the alkyl chain contains about 8 to 16 carbon atoms, and condensates incorporating not more than about 20 ethylene oxide units, are preferred. Suitable alkyl phenols include decyl phenol, dodecyl phenol, tetradecyl phenol and hexadecyl phenol. A nonyl phenol condensate incorporating on average about 8 ethylene oxide units is a particularly preferred material for use in an enzyme-containing granule of the invention.

Although not preferred, other types of nonionic detergent-active compounds may be used if desired. Examples of these include alkyl amides of aliphatic carboxylic acids containing from 8 to 18 carbon atoms; alkanolamides of such aliphatic carboxylic acids; short-chain ethoxylates of such alkanolamides, such as ethoxylates of coconut and tallow ethanolamides containing 2 to 3 ethylene oxide units; polyethylene glycols having molecular weights in the range of about 200 to about 30,000; and polyoxyethylene glyceride esters.

The invention is applicable to the stabilisation of any of the enzymes which are conventionally incorporated, or have been proposed as being suitable for incorporation into a fabric-washing detergent composition. The man skilled in the art of formulating enzymatic fabric-washing detergent compositions will be well aware of the nature of these enzymes, the various types which are commercially available, and which of these types are most suited to his particular needs. However, the following enzymes and commercially-available enzyme products are

especially suitable for use in enzyme-containing granules of the invention.

Although a vast number of different types of enzymes are known, such as oxidoreductases, transferases, desmolases and isomerases, in practice it has been found that the hydrolases are particularly effective in dealing with commonly-encountered domestic laundry soils.

Hydrolases catalyse the addition of water to soil attached to a fabric article, and thereby usually degrade the soil and break up its constituent chemical molecules into smaller units. Under the action of a hydrolase, soil becomes loosened and more readily removable from the fabric to which it is attached. The most common types of hydrolases are proteases, which attack protein-based soils; esterases, which attack lipid soil such as sebum; carbohydrases, which attack carbohydrate soil; and nucleases, which attack nucleic acids encountered in skin residues.

Preferred enzymes for use in a fabric-washing detergent composition of the invention are stable to pH in the range of about 8 to 10, and will perform their catalytic function at any temperature between about 10 and about 60°C.

Many suitable enzymes are available commercially. These are usually in fine powder form, the powder containing from 2 to 80% of active enzyme mixed with one or more inert diluents such as starch, organic clays, sodium sulphate, calcium sulphate and sodium chloride. Alternatively, some enzymes are now becoming available in liquid form, the liquid usually being a slurry of enzyme in nonionic detergent-active material of the type already described.

Table I below lists some of the preferred commercially-available enzyme products. All the enzyme products listed are in powder form.

Table I

Preferred commercially-available enzyme products

Trade Name (RTM indicates that the name is a Registered Trade Mark)	Manufacturer
Alcalase (RTM)	Novo Industri A/S, Copenhagen, Denmark.
Maxatase (RTM)	Gist-Brocades NV, Delft, Holland.
Protease B-4000	Schweizerische Ferment AG, Basle, Switzerland.
Protease AP	
Pronase – P	Kaken Chemical Company, Japan.
Pronase – AS	
Pronase – AF	
Rapidase P-2000 (RTM)	Rapidase, Seclin, France.

Of the above preferred enzyme products, "Alcalase" and "Maxatase" have been found to be particularly well suited for use in enzyme-containing granules of the invention.

Alternatively, an enzyme slurry may be sprayed onto the granulated core material. The enzyme slurry may be obtained commercially as such, or may be prepared by admixture of an enzyme powder and cohesive nonionic detergent.

The spraying may be conducted with the granulated core material contained within a fixed drum incorporating axially-rotating blades to agitate and fluidise the granulated core material. The drum should be vented through a scrubber to collect any solid material, particularly enzymatic material, escaping from the drum. The application of enzyme powder may also be accomplished in the drum.

Alternatively, the spraying may be conducted in a fluidised bed mixer, although this is not preferred due to the greater likelihood of finely-divided solid material escaping from the mixer, particularly if enzyme powder is being used.

The temperature at which the cohesive nonionic detergent, or the enzyme slurry, is sprayed onto the granulated core material will depend on the melting point of the material to be sprayed. As the cohesive nonionic detergents have melting points of less than 30°C, the spraying should be conducted at about 30 to 60°C, preferably about 30 to 40°C.

In the process of the invention, an outer layer of cohesive nonionic detergent, incorporating the polymer is applied to the sprayed granulated core material after the application of the enzyme. This outer layer may be applied using the same apparatus as had been used to prepare the basic sprayed granulated core material. As before, the temperature at which the cohesive nonionic detergent is sprayed depends on its melting point. However, although this is not essential, it has been found advantageous to spray this outer layer of cohesive nonionic detergent at a higher temperature than that used for the earlier spraying. For the nonionic detergent-active compounds of the invention, this outer layer should ideally be applied at a temperature of about 50 to 70°C, preferably about 60 to 65°C.

The granulated core material should comprise from about 45 to about 95%, preferably from about 60 to about 80%, by weight of the enzyme-containing granule.

The inner layer of cohesive nonionic detergent should comprise from about 2 to about 15%,

preferably from about 5 to about 10%, by weight of the enzyme-containing granule. The outer layer of cohesive nonionic detergent should be of similar proportions. These amounts do not include the amount of the polymer present in the enzyme-containing granule.

Where an enzyme powder is used, the amount of enzyme powder should be from about 1 to about 30%, preferably from about 5 to about 20%, by weight of the enzyme-containing granule. The amount of enzyme powder used will be governed by the enzyme activity of the enzyme powder and the level of enzyme activity desired in the enzyme-containing granule itself.

The enzyme slurry (including any diluting nonionic detergent-active material) should comprise from about 3 to about 40%, preferably from about 10 to about 30%, by weight of the enzyme-containing granule.

The enzyme-containing granules of the invention may be incorporated into any conventional particulate fabric-washing detergent composition without any alteration being made to the basic formulation of the detergent composition. The incorporation will be made after the bulk of the detergent composition has been prepared by conventional powder-making processing techniques, such as by spray drying, as the enzyme-containing granules cannot withstand any severe processing conditions. The enzyme-containing granules will generally be dry-dosed into the detergent powder using, for instance, a fluidised bed technique.

The quantity of enzyme-containing granules incorporated in a fabric-washing detergent composition of the invention will be governed by the enzyme activity of the enzyme-containing granules and the level of enzyme activity desired in the detergent composition as a whole. In general, the enzyme-containing granules should be incorporated in the detergent composition in sufficient quantity to provide the equivalent of from about 0.005 to about 5%, preferably from about 0.005 to about 2.5%, by weight of commercially-available enzyme powder or enzyme slurry in the detergent composition. It will usually be sufficient for a detergent composition of the invention to incorporate from about 1 to about 25% by weight of enzyme-containing granules.

In addition to the enzyme-containing granules, a detergent composition of the invention may contain any of the ingredients which are incorporated into conventional fabric-washing detergent compositions in any of the amounts in which such ingredients are commonly used, provided that such ingredients are not unduly detrimental to the essential enzyme activity of the detergent composition. The man skilled in the art of formulating enzymatic detergent compositions will be familiar with the types of ingredients which may or may not be incorporated therein.

A detergent composition of the invention will contain at least one organic detergent-active compound. The organic detergent-active content of the composition will generally be from about 5 to about 50%, preferably from about 5 to about 35%, and particularly preferably from about 10 to about 25%, by weight of the composition. The nature of the organic detergent-active compound or compounds in the composition is not an essential feature of the invention: any of the organic detergent-active compounds conventionally incorporated in or proposed for use in detergent compositions may be used, and those skilled in the art of formulating detergent compositions will be familiar with these organic detergent-active compounds and the various amounts and combinations in which they may advantageously be used. The organic detergent-active compound or compounds may be anionic, nonionic, amphoteric or zwitterionic in character.

Typical anionic detergent-active compounds are water-soluble or water-dispersible salts of various organic acids. The cations of such salts are generally alkali-metals, such as sodium and, less preferably, potassium, but other cations, such as ammonium and substituted ammonium, can be used if desired. Examples of suitable organic acids are: alkyl benzene sulphonic acids, the alkyl chains of which contain from about 8 to about 20 carbon atoms, such as p-dodecyl benzene sulphonic acid and linear alkyl (C_{10-15}) benzene sulphonic acid; the mixtures of sulphonic acids obtained by reacting linear and branched olefins, particularly linear "cracked-wax" or "Ziegler" alpha-olefins, containing from about 8 to about 22 carbon atoms, with sulphur trioxide; alkyl sulphonic acids obtained by reacting alkanes containing from about 8 to about 22 carbon atoms with sulphur dioxide/oxygen or sulphur dioxide/chlorine (followed by hydrolysis in the latter case), or by the addition of bisulphite to olefins, particularly linear "cracked-wax" or "Ziegler" alpha-olefins, containing from about 8 to about 22 carbon atoms; alkyl sulphuric acids obtained by reacting aliphatic alcohols containing from about 8 to about 22 carbon atoms with sulphur trioxide; alkyl ether sulphuric acids, obtained by reacting molar quantities of aliphatic alcohols containing from about 6 to about 18 carbon atoms with from about 1 to about 15 moles of ethylene oxide, or a suitable mixture of ethylene oxide and propylene oxide, and subsequently reacting the alkoxylated alcohol with sulphur trioxide to yield the required acid; and natural or synthetic aliphatic carboxylic acids, particularly those derived from natural sources such as tallows, coconut oil, palm oil, palm kernel oil and groundnut oil.

Many of the nonionic detergent-active compounds hereinbefore described for use in an

enzyme-containing granule of the invention are also suitable for use as detergent-active compounds in a fabric-washing detergent composition incorporating such granules. Further examples of nonionic compounds suitable as detergent-active compounds are: long-chain tertiary amine oxides corresponding to the general formula $R_1R_2R_3N \longrightarrow 0$, wherein R_1 is an alkyl radical containing from about 8 to 18 carbon atoms and R_2 and R_3 are each methyl, ethyl or hydroxy ethyl radicals, such as dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethylhexadecylamine oxide and N-bis (hydroxyethyl) dodecylamine oxide; long-chain tertiary phosphine oxides corresponding to the general formula $RR'R''P \longrightarrow 0$, wherein R is an alkyl, alkenyl or monohydroxyalkyl radical containing from 10 to 18 carbon atoms and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms, such as dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, dimethylstearylphosphine oxide, ethylpropylcetylphosphine oxide, diethyldodecylphosphine oxide, bis (hydroxymethyl) dodecylphosphine oxide, bis (2-hydroxyethyl) dodecylphosphine oxide, 2-hydroxypropylmethyltetradecylphosphine oxide, dimethyloleylphosphine oxide and dimethyl-2-hydroxydodecylphosphine oxide; and dialkyl sulphoxides corresponding to the general formula $RR'S \longrightarrow 0$, wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxyalkyl radical containing one or two other oxygen atoms in the chain, the R groups containing from 10 to 18 carbon atoms and wherein R' is methyl, ethyl or alkylol radical, such as dodecyl methyl sulphoxide, tetradecyl methyl sulphoxide, 3-hydroxytridecyl methyl sulphoxide, 2-hydroxydodecyl methyl sulphoxide, 3-hydroxy-4-dodecyloxybutyl methyl sulphoxide, 2-hydroxy-3-decyloxypropyl methyl sulphoxide, dodecyl ethyl sulphoxide, 2-hydroxydodecyl ethyl sulphoxide and dodecyl-2-hydroxyethyl sulphoxide.

Examples of suitable amphoteric detergent-active compounds are: derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilising group, such as sodium-3-dodecylaminopropionate, sodium-3-dodecylaminopropanesulphonate and sodium N-2-hydroxydodecyl-N- methyltaurate.

Examples of suitable zwitterionic detergent-active compounds are: derivatives of aliphatic quaternary ammonium compounds, sulphonium compounds and phosphonium compounds in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilising group, such as 3-(N,N-dimethyl-N-hexadecyl-ammonium) propane-1-sulphonate betaine, 3-(N,N-dimethyl-N-hexadecyl-ammonium)-2-hydroxypropane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium) propane-1-sulphonate betaine, and 3-(cetylmethylphosphonium) ethane sulphonate betaine.

Further examples of suitable detergent-active compounds commonly used in the art are given in "Surface Active Agents, Volume I" by Schwartz and Perry (Interscience 1949) and "Surface Active Agents, Volume II" by Schwartz, Perry and Berch (Interscience 1958).

In general, a detergent composition will contain one or more detergency builders. Usually the total amount of detergency builders in a detergent composition of the invention will be from about 5 to about 70% by weight of the detergent composition. Many detergency builders are known, and those skilled in the art of formulating fabric-washing detergent compositions will be familiar with these materials. Examples of known detergency builders are sodium tripolyphosphate; sodium orthophosphate; sodium pyrophosphate; sodium trimetaphosphate; sodium ethane-1-hydroxy-1,1-diphosphonate; sodium carbonate; sodium silicate; sodium citrate; sodium oxydiacetate; sodium nitrilotriacetate; sodium ethylenediaminetetraacetate; sodium salts of long-chain dicarboxylic acids, for instance straight chain (C_{10} to C_{20}) succinic acids and malonic acids; sodium salts of alpha-sulphonated long-chain monocarboxylic acids; and modified starches such as starches oxidised, for example using sodium hypochlorite, in which some anhydroglucose units have been opened to give dicarboxyl units.

A detergent composition of the invention may also contain additional conventional detergent composition ingredients, in any of the amounts in which such conventional ingredients are usually employed, for instance lather boosters, such as coconut monoethanolamide and palm kernel monoethanolamide; lather controllers; fillers, usually inorganic salts such as sodium sulphate and magnesium sulphate; bleaching agents such as sodium perborate, sodium percarbonate, trichloroisocyanuric acid, and sodium and potassium dichloroisocyanurates; bleach precursors; bleach activators; antiredeposition agents, such as sodium carboxymethylcellulose; and, usually present only in minor amounts, perfumes, colourants, fluorescers, corrosion inhibitors and germicides.

A detergent composition of the invention can be prepared using any of the conventional manufacturing techniques commonly used or proposed for the preparation of detergent compositions, such as slurry-making followed by spray-drying or spray-cooling, and subsequent dry-dosing of sensitive ingredients not suitable for incorporation prior to the drying

step. Other conventional techniques, such as noodling, granulation, and mixing by fluidisation in a fluidised bed, may be utilised as and when necessary. Such techniques are familiar to those skilled in the art of detergent composition manufacture.

By using such conventional manufacturing techniques, a detergent composition of the invention may be prepared in any of the common particulate physical forms associated with fabric-washing detergent compositions, such as powder, flakes, granules or noodles, and such particulate forms compressed into tablet form.

The invention is illustrated in the following Examples. It should be noted that, although each Example is self-consistent, it is not possible to compare the half-life results obtained in one Example with those obtained in another separate Example, even where apparently similar Control compositions were employed, due to variability in the storage properties found between different batches of the base compositions.

EXAMPLES 1 TO 3

Three samples of enzyme-containing granules were prepared according to the invention by spraying nonylphenol, condensed with 8 moles of ethyleneoxide (a nonionic detergent-active compound sold under the registered trade mark Conox J089) at about 30 to 40°C onto granulated anhydrous sodium tripolyphosphate in a drum incorporating axially-rotating blades, dusting the sprayed granules with a commercially-available enzyme powder (sold under the registered trade mark "Alcalase"), and finally spraying the granule at about 60 to 65°C with a mixture of the same nonionic detergent-active compound and an ethylene-maleic anhydride copolymer (sold under the trade name "EMA 11"). Enzyme-containing granules incorporating no copolymer (Comparative Example A) were also prepared. The final compositions of the enzyme-containing granules were:

Component	% (by weight of the finished granule)			
	Example 1	Example 2	Example 3	Comparative Example A
Anhydrous sodium tripolyphosphate	70	70	70	70
Inner nonionic layer	7	7	7	7
"Alcalase" enzyme powder	15	15	15	15
Outer nonionic layer	7.5	7	6.5	8
"EMA 11" copolymer	0.5	1	2	—

EXAMPLE 4

The enzyme-containing granules of Example 2, incorporating 1.0% of the ethylene-maleic anhydride copolymer, were dry-dosed into a conventional fabric-washing detergent powder using a fluidised bed mixer. The resultant detergent powder had the following essential formulation:

Component	% (by weight)
Sodium alkyl benzene sulphonate (sulphonated DOB/055 obtained from Shell)	14
Anhydrous sodium soap	2
Palm kernel ethanolamide	2
Sodium tripolyphosphate	29
Anhydrous alkaline sodium silicate	7
Anhydrous sodium sulphate	7
Sodium toluene sulphonate	1
Sodium carboxymethyl cellulose	0.5
Sodium perborate	25
Enzyme-containing granules	5
Fluorescers, perfumes, water, to	100

As a comparative Example (B), an identical detergent powder was prepared incorporating the enzyme-containing granules of Comparative Example A.

The two detergent powders were stored at 37°C in closed containers, and the half life of the enzyme activity was determined. Enzyme activity was measured by determining the number of glycine units produced from casein by a known quantity of the enzyme under test, using a fresh sample of the enzyme as a standard. The following results were obtained:

TABLE II

Detergent Powder	Half life (days) of enzyme activity
Example 4	17
Comparative Example B	9

These results show that the incorporation of the ethylene-maleic anhydride copolymer in the enzyme-containing granules in the detergent powder of Example 4 almost doubled the half life of the enzyme activity, even under the severe storage conditions used.

Two further samples of these two detergent powders were stored in laminated packets at 28°C/70% RH, and the following half lives for the enzyme activity were determined:

TABLE III

Detergent Powder	Half life (days) of enzyme activity
Example 4	75
Comparative Example B	50

28°C/70% RH are more severe than any conditions likely to be encountered during normal storage of a detergent composition. The improved stability of the enzyme activity associated with an enzyme-containing granule is maintained under these conditions, and under normal storage conditions an even longer half life is obtained.

EXAMPLE 5

Two samples of enzyme-containing granules having the following compositions were prepared by the method described for Examples 1 to 3:

Component	% (by weight of the finished granule)	
	Example 5	Comparative Example C
Anhydrous sodium tripolyphosphate	75	75
Inner nonionic layer	6	6
"Maxatase" enzyme powder	10	10
Outer nonionic layer	7	9
"EMA 11" copolymer	2	—

The nonionic detergent-active compound used was the same as that used in the previous Examples.

EXAMPLE 6

The enzyme-containing granules of Example 5 and Comparative Example C were dry-dosed at a level of 5% by weight into two samples of the same conventional detergent powder as was used in Example 4. The two resultant detergent powders were designated Example 6 and Comparative Example D respectively, and were stored at 28°C/70% RH in laminated packets. The following enzyme activity half lives were determined:

TABLE IV

Detergent Powder	Half life (days) of enzyme activity
Example 6	110
Comparative Example D	75

These results indicate that the invention is applicable to the enzyme product "Maxatase".

EXAMPLE 7

Enzyme-containing granules prepared according to Example 3 and Comparative Example A were dry-dosed at a level of 5% by weight into two samples of a conventional nonionic-based fabric-washing detergent powder having the following formulation:

Component	% (by weight)
Nonionic detergent-active compound (sec. C_{11}—C_{15} linear alcohol condensed with 9 moles of ethylene oxide)	12
Anhydrous sodium soap	2
Palm kernel fatty acid monoethanolamide	2
Sodium tripolyphosphate	35
Anhydrous alkaline sodium silicate	5
Sodium toluene sulphonate	1
Sodium carboxymethyl cellulose	0.5
Sodium perborate	20
Sodium sulphate, fluorescers, water, to	100

The two dosed detergent powders were designated Example 7 and Comparative Example E respectively, and were then tested as in Example 6. The following enzyme activity half lives were obtained:

TABLE V

Detergent Powder	Half life (days) of enzyme activity
Example 7	46
Comparative Example E	35

These results indicate that, although enzymes are inherently less stable in nonionic-based detergent powders, the stability improvement of the invention is still maintained.

EXAMPLE 8

Enzyme-containing granules prepared according to Example 5 and Comparative Example C were dry-dosed at a level of 5% by weight into two samples of the same nonionic-based detergent powder used in Example 7. The two dosed detergent powders were designated Example 8 and Comparative Example F respectively, and were tested as in Example 7. The following enzyme activity half lives were obtained:

TABLE VI

Detergent Powder	Half life (days) of enzyme activity
Example 8	90
Comparative Example F	75

These results show that the stability improvement of the invention is obtained for the enzyme product "Maxatase" in a nonionic-based detergent powder.

WHAT WE CLAIM IS:—

1. An enzyme-containing granule comprising a core of carrier material which is a solid, water-soluble inorganic alkali metal salt, an enzyme, affixed to the core by means of a cohesive nonionic detergent with a melting point in the range of 0–30°C enrobing the core, and an enrobing outer layer comprising a polymer of an unsaturated mono- or polycarboxylic acid as hereinbefore defined, the polymer being present in an amount of from 0.1 to 5% by weight of the granule.

2. An enzyme-containing granule according to claim 1, wherein the polymer comprises from about 0.5 to about 3% by weight of the granule.

3. An enzyme-containing granule according to claim 1 or claim 2, wherein the polymer is a copolymer of an unsaturated polycarboxylic acid and/or its anhydride with an alpha-olefin or a vinyl compound.

4. An enzyme-containing granule according to claim 3, wherein olefin is ethylene.

5. An enzyme-containing granule according to claim 3 or claim 4, wherein the unsaturated polycarboxylic acid is in the form of its anhydride.

6. An enzyme-containing granule according to claim 5, wherein the anhydride is maleic anhydride.

7. An enzyme-containing granule according to any of the preceding claims, wherein the polymer has a molecular weight of from about 10,000 to about 500,000.

8. An enzyme-containing granule according to any of claims 1–7, wherein the nonionic-detergent has a melting point in the range of 15 to 25°C.

9. An enzyme-containing granule according to any of claims 1–8, wherein the nonionic detergent is an ethoxylated C_8—C_{18} aliphatic alcohol containing from 5 to 20 ethylene oxide units.

10. An enzyme-containing granule according to any of the preceding claims, wherein the core material is sodium tripolyphosphate.

11. An enzyme-containing granule according to any of the preceding claims, wherein the enzyme is incorporated in the granule in the form of an enzyme powder and is bound to the core by a layer of cohesive nonionic detergent, and in which granule the polymer is contained within an outer layer of cohesive nonionic detergent.

12. An enzyme-containing granule according to claim 1, substantially as hereinbefore described with reference to any of the Examples.

13. A fabric-washing detergent composition incorporating from 1 to 25% by weight of enzyme-containing granules according to any of the preceding claims.

14. A fabric-washing detergent composition according to claim 13, substantially as hereinbefore described with reference to any of the Examples.

15. A process for the preparation of an enzyme-containing granule according to any of claims 1–10, wherein cohesive nonionic detergent is sprayed at a temperature of 30 to 60°C onto granulated core material, the sprayed granules are dusted with an enzyme powder, and an outer layer of cohesive nonionic detergent incorporating the polymer is sprayed onto the dusted granules at a temperature of 50 to 70°C.

16. A process for the preparation of an enzyme-containing granule according to claim 1, substantially as hereinbefore described.

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